Ammonium molybdophosphate impregnated alumina microspheres as a new generation sorbent for chromatographic ^{137}Cs/^{137m}Ba generator

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ABSTRACT

Barium-137m availed from a ^{137}Cs/^{137m}Ba generator is an attractive industrial radiotracer for liquid flow rate measurement owing to its short half-life ($T_{1/2} = 2.5$ min) and emission of highly energetic gamma radiation ($E_\gamma = 661.7$ keV). Ammonium molybdophosphate (AMP) impregnated alumina microspheres (AMP-Al$_2$O$_3$), an engineered form of sorbent material was synthesized by Gel Entrapment Technique (GET). The utility of the material in the preparation of ^{137}Cs/^{137m}Ba generator was evaluated. Various experimental parameters were optimized for efficient retention of ^{137}Cs and selective elution of ^{137m}Ba. A chromatographic 0.74 GBq (20 mCi) ^{137}Cs/^{137m}Ba generator was developed using this material and its performance was evaluated for 6 months. Barium-137m could be eluted from the generator using 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ solution with >80% yield and with acceptable radionuclidic purity suitable for industrial radiotracer investigations.

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1. Introduction

The technical, economic and environmental benefits of the radiotracer technology have been well demonstrated and recognized by the industrial sectors. The use of short-lived gamma-emitting radiotracer can be valuable for numerous industrial applications [1]. Ensuring timely availability of short-lived radiotracers at the industrial site is the main hurdle towards use of radiotracer techniques in industries. A convenient availability of short-lived radiotracer, without the expense of an on-site cyclotron or reactor facilities lies in the utilization of a radioisotope generator. The generator can also be used in tracer studies in emergency situations, routine inspections and process control, especially in remote areas as well as for repeated tracer studies in pilot plants and laboratories.

There is a great deal of interest in the use of ^{137m}Ba ($T_{1/2} = 2.5$ min) as an industrial radiotracer due to its energetic gamma emission ($E_\gamma = 661.7$ keV, 85.12%) [2]. The short half-life of the ^{137m}Ba has been cited as an advantage, leading to multiple elutions from a single generator and facilitating repeated studies on the same subject within a short time interval. It eliminates concerns about site contamination, environmental persistence, and waste disposal issues. The ^{137}Cs/^{137m}Ba generator has emerged as the most popular source for availing ^{137m}Ba. The long half-life

($T_{1/2} = 30$ y) of the parent radionuclide ^{137}Cs ensures convenient availability of ^{137m}Ba for long periods of time. Barium-137m is a very useful radiotracer for liquid flow rate measurement [3,4] because of its highly energetic gamma ray which can be easily detected outside the pipes. It is also possible to install the generator into an industrial assembly to provide continuous supply of ^{137m}Ba tracer into the process stream for flow rate measurement.

The ^{137}Cs/^{137m}Ba generators available commercially are of very low activity (typically 370 kBq), intended for the demonstration purposes in academic institutions. The current demand for the ^{137}Cs/^{137m}Ba generator of durable construction, amenable for industrial applications is perceived to be rather small to make its commercial production economically attractive. Concerted efforts are therefore necessary to undertake the development of ^{137}Cs/^{137m}Ba generators in order to realize the scope of accessing ^{137m}Ba in several MBq quantities for industrial radiotracer studies.

Several column chromatographic ^{137}Cs/^{137m}Ba generator systems using variety of inorganic exchangers have been reported over the past several years [5–15]. Out of these ion-exchangers, ammonium molybdophosphate (AMP) received the maximum attention owing to its high specificity towards Cs$^+$ ion and stability in the radioactive media [16]. However, AMP has a microcrystalline structure having particle size in the range of 1–5 μm [17–25] which is impervious to liquid, thereby rendering it unsuitable for use in column application in pure form. In order to overcome the problems associated with fine particle size, the AMP particles must be engineered into an acceptable granular form. During the last two decades, several techniques to fix AMP on different

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supporting matrices such as asbestos [18], silica gel [26], Amberlite XAD-7 [27], polyacrylonitrile (PAN) [28,29], calcium alginate [30], cenospheres [31] and Al_2O_3 [32,33] have been developed to make engineered forms of materials suitable for column operations. Out of these, AMP–PAN has been extensively studied and used for the removal of ^{137}Cs from high level acidic radioactive waste at Idaho National Engineering and Environmental Laboratory (INEEL), USA [34–36]. Although granulated AMP containing organic materials as supporting matrices provides excellent flow characteristics, issues regarding the potential radiation degradation of the polyacrylonitrile (PAN) binder under long-term use are yet to be addressed. The degradation of organic materials would result in ^{137}Cs breakthrough in the ^{137m}Ba eluate, which in turn would interfere in radiotracer investigations. In view of the above described drawbacks, use of inorganic matrix to make an engineered form of AMP is ideally suited for such type of applications.

In this context, the use of AMP-Al_2O_3 microspheres developed by our group [32] using Gel Entrapment Technique (GET), as a column matrix for chromatographic $^{137}Cs/^{137m}Ba$ generator deemed worthy of consideration. The inorganic back bone of the microsphere could be of valuable attribute towards the preparation of a chromatographic $^{137}Cs/^{137m}Ba$ generator suitable for industrial radiotracer applications. In this communication, we describe the overall synthesis procedure, structural characterization, sorption properties assessment, development of AMP-Al_2O_3 based $^{137}Cs/^{137m}Ba$ generator, evaluation of long-term operation and assessment of the quality of the separated ^{137m}Ba for industrial radiotracer applications.

2. Materials and methods

2.1. Materials

Reagents including nitric acid, ammonium hydroxide, etc. were of analytical grade and were procured from S.D. Fine Chemicals, Mumbai, India. Ammonium nitrate, aluminum nitrate, ammonium molybdate, hexamethylenetetramine (HMTA), urea, and citric acid were of analytical grade and obtained from E. Merck, Mumbai, India. Radioisotopes such as ^{137}Cs, ^{134}Cs and ^{133}Ba were available in the Radiopharmaceuticals Division, BARC.

2.2. Equipments

A mechanical wrist-action shaker (Secor, India) was used for batch equilibrium studies. An HPGe Multichannel analyzer (coaxial photon detector system, Canberra Eurisys, France) with a 0.5 keV resolution and range from 1.8 keV to 2 MeV was used for gamma spectrometric analysis and also for quantitative estimation. The trace level of metal contaminations was estimated using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-ES JY-238, Emission Horiba Group, France). Standard ^{152}Eu source of known strength was used for efficiency calibration of the detector. The activity of ^{133}Ba and ^{134}Cs were measured by γ-spectrometry by the quantification of 356 keV and 605 keV photo peaks, respectively. All samples were counted at the same geometry.

2.3. Synthesis of AMP

Ammonium molybdophosphate (AMP) used in this work was synthesized adopting the reported citromolybdate procedure [20]. A solution containing a mixture of citric acid (81 g), ammonium nitrate (81 g) and ammonium paramolybdate (102 g) in 2 L of distilled water was poured into 2 L nitric acid solution (7 M) in a 5 L capacity beaker with constant stirring. Then, 10 mL of 5% solution of diammonium hydrogen phosphate was added slowly to this reaction mixture and the mixture was heated to boiling. The precipitate

thus formed was allowed to settle down and subsequently it was filtered and dried under infrared lamp at ~60 °C.

2.4. Synthesis of the gel spheres (AMP-Al_2O_3)

A broth solution was prepared by mixing AMP powder with a solution containing 1.4 M aluminum nitrate, 1.54 M urea and 1.54 M hexamethylenetetramine at a temperature of 5 °C. The droplets of this broth were passed through hot silicone oil at 95 °C during which they gelled [37]. The spheres were separated from the oil, degreased with carbon tetrachloride (CCl_4) and then washed thoroughly with 0.1 M NH_4OH solution followed by washing with deionized water to remove the chemical impurities that might have percolated inside the spheres. The washed gels were then calcined at 200 °C, 300 °C and 380 °C for 10 h. After thermal treatment, the prepared gel particles were cured in ambient temperature for 24 h under vacuum.

In order to estimate the AMP content in the gel, 1 g of the material was crushed in an agate mortar using a pestle. The powder obtained was treated with 2 M NaOH solution in which AMP got dissolved. This solution was filtered and the filtrate was acidified. On acidification, AMP got precipitated and the amount of precipitate was estimated gravimetrically.

2.5. Chemical stability of AMP-Al_2O_3 microspheres

The chemical stability of the AMP-Al_2O_3 sorbent prepared was assessed in HNO_3 and NH_4NO_3 solution of strength 0.1–6 M. A weighed amount of the sorbent material (1 g) was placed in 50 mL solvent of interest and kept for 24 h with continuous shaking at room temperature. Subsequently it was filtered and the level of Al and Mo metal ions in the filtrate was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

2.6. Determination of the distribution ratios (K_d) of Cs^+ and Ba^{2+} ions

The distribution ratios (K_d) of Cs^+ and Ba^{2+} ions for the AMP-Al_2O_3 matrix were measured at different acid concentrations, using ^{134}Cs and ^{133}Ba as radiotracers. In each experiment, 200 mg of sorbent was suspended in 20 mL solution containing the radioactive metal ions, in a 50 mL stoppered conical flask. The flasks were shaken in a wrist arm mechanical shaker for 1 h at 25 °C and then filtered. An aliquot of the solution before and after equilibration were measured in a well type NaI(Tl) counter using appropriate window ranges (300–400 keV for ^{133}Ba and 600–650 keV for ^{134}Cs). The distribution ratios were calculated using the following expression:

$$K_d = \frac{(A_i - A_{eq})V}{A_{eq}m} \text{L g}^{-1}$$

where A_i is the initial total radioactivity of 1 mL of the solution, A_{eq} is the unadsorbed activity in 1 mL of the solution at equilibrium, V is the solution volume (cm^3) and m is the mass (g) of the sorbent. All measurements were carried out at 25 °C in triplicate.

2.7. Determination of sorption capacity of AMP-Al_2O_3

2.7.1. Static sorption capacity

The static sorption capacity of the sorbent (AMP-Al_2O_3) for Cs^+ ions was determined by batch equilibration method. For this, 50 mL of cesium nitrate solution (1 mg Cs mL^{-1}) prepared in double distilled water was taken in a flask. The solution was then spiked with ~10 μCi (370 kBq) of ^{134}Cs. A known amount of sorbent material (here 0.5 g of AMP-Al_2O_3) was added to the flask and the mixture was kept in a shaker for ~1 h at room temperature. The activity of

^{134}Cs was estimated by using a HPGe detector coupled to a multi-channel analyzer, by measuring the counts at 605 keV and 796 keV photopeaks corresponding to ^{134}Cs. The unadsorbed ^{134}Cs activity in the solution was measured and the percentage of ^{134}Cs adsorbed was calculated. All measurements were carried out at 25 °C in triplicate.

2.7.2. Breakthrough pattern and dynamic sorption capacity

In order to study the sorption pattern of Cs$^+$ ions under dynamic conditions in a fixed bed ion-exchange column, a borosilicate glass column of dimension 15 cm × 0.4 cm (i.d.) with sintered disc (G_0) at the bottom was packed with 1 g of the synthesized sorbent. After the column was conditioned with 2 M HNO$_3$, 25 mL of cesium nitrate solution (of concentration 1.0 mg Cs mL^{-1}) in 2 M HNO$_3$, spiked with ^{134}Cs tracer [370 kBq (10 μCi)] was allowed to pass through the column at a rate of 0.25 mL min^{-1}. 1 mL of this solution was kept as reference (C_0). The effluent was collected in fractions of 1 mL aliquots (C). The ^{134}Cs activity in the reference (C_o) and effluent fractions was determined by measuring the 796 keV γ-ray peak of ^{134}Cs in a HPGe detector. The ratio of the count rate 'C' of each 1 mL effluent to the count rate 'C_o' of 1 mL of the original feed Cs solution was taken as the parameter to follow the sorption pattern.

In order to optimize the volume of the feed required for the near quantitative loading of ^{134}Cs activity in the generator column, sample solutions of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mL containing 5 mg of Cs (as CsNO$_3$) were prepared. These solutions were spiked with 37 kBq (1 μCi) mL^{-1} of ^{134}Cs and then passed through the column of dimension 15 cm × 0.4 cm (i.d.) containing 1 g of the sorbent at a flow rate of 0.5 mL min^{-1}. The activities of ^{134}Cs in the solution before and after absorption were estimated gamma spectrometrically by measuring the 796 keV γ-ray peak of ^{134}Cs in a HPGe detector and the amount of Cs retained by the column was assayed.

2.8. Elution behavior of ^{137m}Ba

In order to portray the elution behavior of ^{137m}Ba in a column containing 4.6 GBq (125 mCi) of ^{137}Cs, simulated experiment was carried out by loading 5 mg of inactive carrier Cs spiked with 37 kBq (1 μCi) mL^{-1} of ^{137}Cs in 2 M HNO$_3$, in a chromatographic column containing 1 g of the sorbent. The specific activity of ^{137}Cs is about 925 GBq (25 Ci)/g. Therefore 5 mg of Cs carrier is equivalent to ∼4.6 GBq (125 mCi) of ^{137}Cs. The column was then washed with 10 mL of 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ solution. After allowing growth of ^{137m}Ba (10–15 min), it was eluted with a mixture of 0.1 M NH$_4$NO$_3$ in 0.01–0.5 M HNO$_3$ at a flow rate of 2 mL min^{-1}. Aliquots of the eluate in 1 mL fractions were collected and then subjected to gamma spectrometric analysis using HPGe detector coupled with a multichannel analyzer.

The eluates containing ^{137m}Ba were monitored for appropriate time at a suitable geometry and the counts acquired under the 662 keV photopeak immediately after elution were used for assay of ^{137m}Ba activity. Owing to the very short half-life of ^{137m}Ba (2.5 min), the elution yield (Y) of ^{137m}Ba in each eluted sample was calculated by the relationship [38]

$$Y = \frac{A_{elut}}{(A_{Cs-137}(1 - e^{-\lambda_2 t_s})e^{-\lambda_2 t_w})} \times 100$$

where A_{elut} was the counting-rate (cpm) of 1 mL ^{137m}Ba eluate fraction after correction for ^{137m}Ba decay during 1 min of counting time (i.e. $A_{elut} = A/0.76$, where A is the observed counting rate over 1 min), A_{Cs-137} was the total counting rate (cpm) of ^{137}Cs loaded onto the column in radioactive equilibrium with its daughter ^{137m}Ba, t_s was the collection time (s) of a 1 mL sample during elution, t_w was the

waiting time (s) before starting measurement of the sample, λ_2 was the decay constant of ^{137m}Ba (4.529 × 10^{-3} s^{-1}).

2.9. Preparation of ^{137}Cs/^{137m}Ba generator

A borosilicate glass column of dimension 8 cm × 0.6 cm (i.d.) with a sintered disc (G_0) at the bottom was packed with 2 g of AMP-Al$_2$O$_3$ and kept in a lead shielded container. It was pre-conditioned with 2 M HNO$_3$ solution. A schematic diagram of the ^{137}Cs/^{137m}Ba generator system is shown in Fig. 1. All the operations were carried out in the closed cyclic system using connecting tubes. Input/output connections were made with standard Teflon tubings of 1 mm inner diameter and connectors. The generator column, connectors and connection tubings were integrated within a small portable lead shielded unit throughout experimental use for radioprotection purpose. Only the elution vial and output vial were accessible externally. The whole system along with the lead shielding assembly was placed on a tripod stand made of steel for the safety and stability. The ^{137}Cs/^{137m}Ba solution containing 740 MBq (20 mCi) of ^{137}Cs at 2 M HNO$_3$ was percolated into the column maintaining a flow rate of 0.25 mL min^{-1}. The ^{137}Cs loaded column was dried under vacuum for 1 min and washed with 100 mL of 2 M HNO$_3$ solution. ^{137m}Ba was regularly eluted from the loaded column with 2 mL of 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ solution in a collection vial having protective lead shield. The elution process can be interrupted at any time by simply disconnecting the collection vial from the generator column. The performance of the generator was evaluated for 6 months. For shipment of the generator column, both the ends of the column were sealed by lead plugs fitted with screwed clamps.

Neutralization of the acidic eluent was accomplished by the addition of equal amount of 0.5 M NaOH in the collection vial with the help of a syringe. Neutralization of the acidic eluate was necessary to avoid the change in pH of the process stream during radiotracer investigation. Maintaining the pH of the process stream is of paramount importance for any radiotracer investigation so as to avoid the adsorption of radiotracer on the vessel, pipe wall, soil or in suspended matter. In some cases, the decrease in pH of the process stream promotes the surface adsorption of tracer along the path and would give erroneous result. The radiotracer could be used as quickly as possible by withdrawing the solution from the sealed vial with the help of a syringe. In this way, ^{137m}Ba obtained from the generator could be used for radiotracer investigations.

3. Results

In order to realize the potential utility of AMP-Al$_2$O$_3$ microspheres as a column matrix for the chromatographic separation of ^{137m}Ba from ^{137}Cs, a thorough optimization of various experimental parameters was found essential. Most of the work was devoted to identify the most favorable conditions from the point of view of elution yield and radionuclidic purity of ^{137m}Ba, reproducibility and long-term operation of the generator.

3.1. Preparation of the AMP-Al$_2$O$_3$ microspheres

The material obtained was a dry yellow powder. In order to prevent the decomposition of AMP, the gel particles were heated to a temperature below 400 °C. Curing of the gel particles was important in order to achieve excellent acid stability. The washing scheme described in the procedure results in minimum loss of AMP. The effect of calcination temperature on the stability of AMP-Al$_2$O$_3$ composite is depicted in Table 1. It was found that the gel obtained on heating to 380 °C was most suitable owing to its high stability in HNO$_3$. The synthesis method is effective, reliable and reproducible. The product consisted of yellow hard porous spheres of nearly uniform size, amenable for column chromatographic operations. The
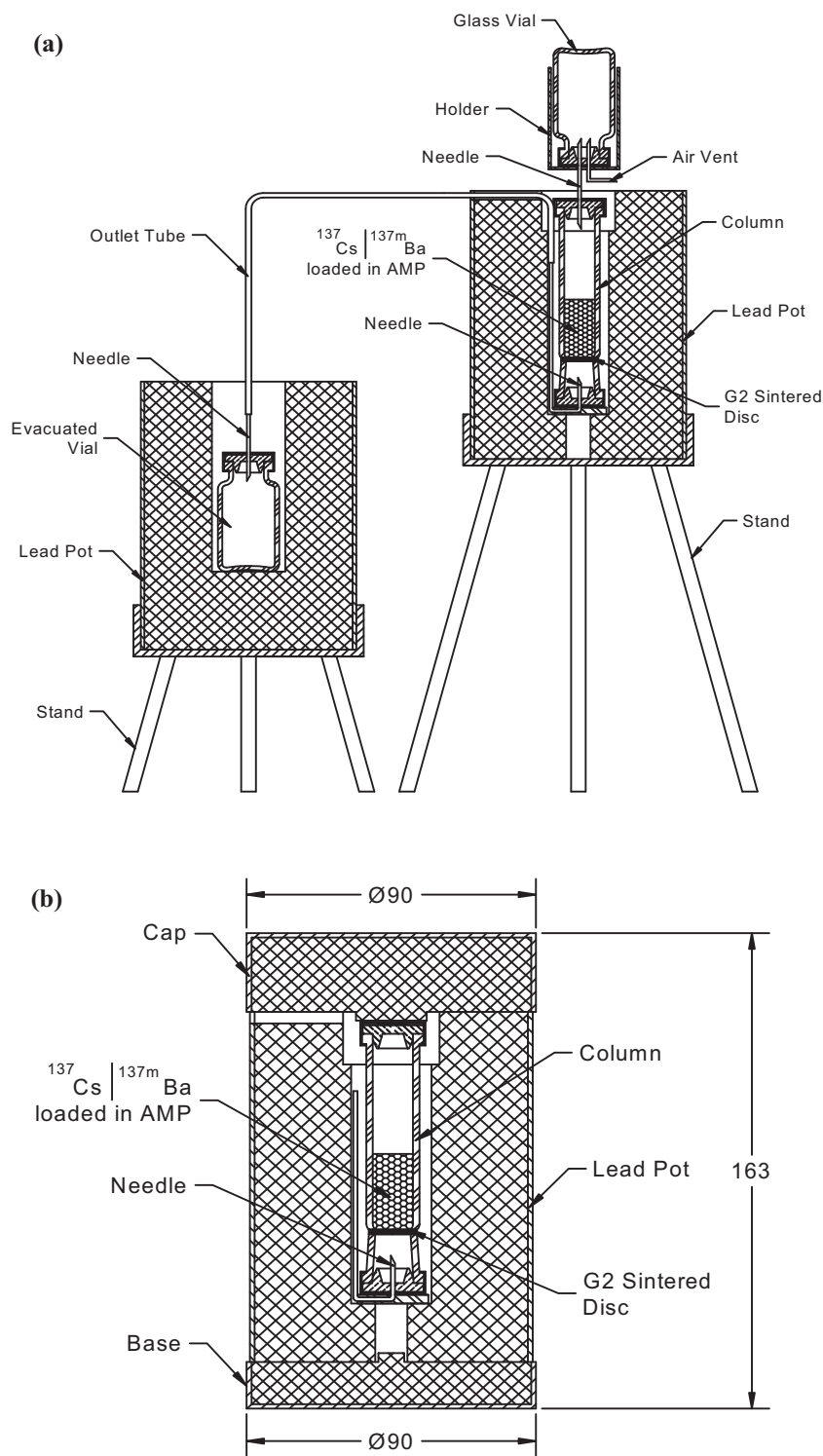
Fig. 1. $^{137}Cs/^{137m}Ba$ generator in a lead shielding assembly (a) during operation and (b) during storage.

Table 1
Effect of temperature on the stability of the AMP-Al$_2$O$_3$ composite.

Calcination temperature (°C)	Stability of AMP-Al$_2$O$_3$ when immersed for 24 h in		
	0.1 M HNO$_3$	1.0 M HNO$_3$	2.0 M HNO$_3$
200	Peptize	Peptize	Peptize
300	Peptize	Peptize	Peptize
380	Peptize	Stable	Stable

Table 2
Distribution ratios (K_d) of Cs^+ ions on AMP and AMP-Al_2O_3 in HNO_3.

HNO_3 concentration (M)	Distribution ratio (K_d)	
	Pure AMP	AMP trapped alumina gel (AMP-Al_2O_3)
0.1	25,793 ± 1025	16,968 ± 1018
0.2	25,181 ± 701	16,062 ± 806
0.5	8075 ± 394	7253 ± 318
1.0	7139 ± 307	6739 ± 285
2.0	6438 ± 105	5865 ± 235
3.0	861 ± 53	771 ± 33
4.0	725 ± 21	659 ± 32
5.0	621 ± 19	538 ± 21
6.0	523 ± 15	431 ± 18
7.0	461 ± 12	389 ± 15
8.0	303 ± 1	317 ± 12

'±' Standard deviation, $n = 3$.

yield per cycle was ∼8 g. The procedure was repeated 10 times to obtain 75–80 g of AMP.

The calculated weight of AMP retained in the dried gels was 0.16 ± 0.02 g per g of the exchanger (AMP-Al_2O_3). Although ∼16 wt% AMP could be loaded on Al_2O_3 by GET technique, the sorbent demonstrated excellent flow performance when used in a chromatographic column and showed potential for long-term generator operation.

3.2. Chemical stability of the AMP-Al_2O_3 microspheres

The short half-life of the ^{137m}Ba provides an opportunity for repeated elutions of the radioisotope from the generator on a daily basis. In order to obtain reproducible chemical purity of ^{137m}Ba throughout the day, the stability of the sorbent during the elution is important. Therefore, it was essential to evaluate the stability of the sorbent over a period of 1 day. The AMP-Al_2O_3 matrix was insoluble in water and chemically inert to HNO_3 and NH_4NO_3 solutions (0.1–6 M) as <1 ppm levels of Al and Mo ions were detected in the filtrate in all the cases, when analyzed by ICP-AES. This characteristic shows that the sorbent can be safely used for generator preparation.

3.3. Determination of distribution ratios (K_d) of Cs^+ and Ba^{2+} ions

In order to obtain optimum separation, the distribution ratio (K_d) values of Cs^+ ions for pure AMP and AMP-trapped alumina spheres (AMP-Al_2O_3) were determined at various acidities of HNO_3 and the results are summarized in Table 2. It is evident from the result that the K_d values obtained with AMP-Al_2O_3 were less when compared with that of pure AMP in nitric acid medium. Although the K_d values of Cs^+ ions on AMP-Al_2O_3 were on lower side, they were adequate to provide considerable selectivity for ^{137}Cs.

A plot of log K_d vs log [H^+] is shown in Fig. 2 which shows that K_d values fall marginally up to an acidity of 2 M; thereafter decreases linearly with a slope of −1 indicating that at acidity greater than 2 M, Cs^+ undergoes exchange with H^+. This behavior is similar to that reported with pure AMP [22]. This confirms that Al_2O_3 content in the matrix does not alter the ion-exchange characteristic of AMP.

The distribution ratio values (K_d) of Cs^+ and Ba^{2+} ions at various acidities are shown in Table 3. The ion-exchangers based on AMP are stable in moderately concentrated acid. At 0.1 M and 0.2 M HNO_3, though the K_d values of Cs^+ and Ba^{2+} ions are favorable to perform their separation, the sorbent tends to peptize in these solutions of low acidity and inhibits the flow of eluent during column operation especially on repeated elution [39]. This property of the ion exchanges impelled us to turn our attention towards 2 M HNO_3. It is seen that Cs^+ ions were taken up by the sorbent at all the
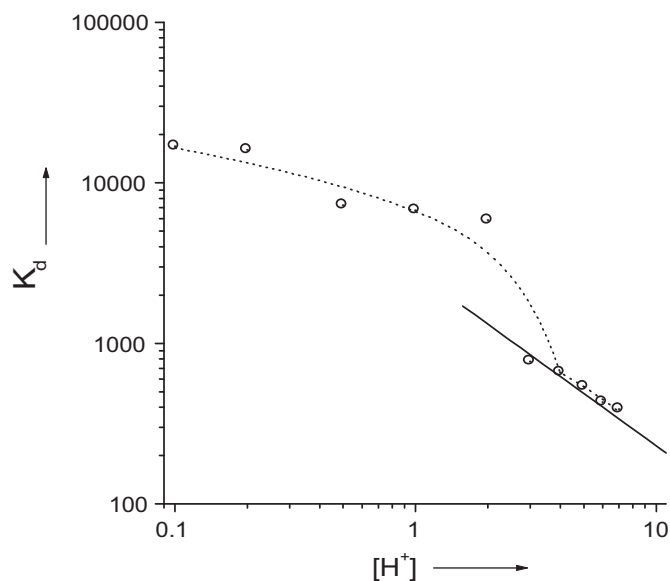

Fig. 2. Variation of K_d of Cs^+ ions on AMP-Al_2O_3 with HNO_3 concentration.

Table 3
Distribution ratios (K_d) of Cs^+ and Ba^{2+} ions on AMP-Al_2O_3 in HNO_3.

HNO_3 concentration (M)	Distribution ratio (K_d)	
	Cs^+	Ba^{2+}
0.1	16,968 ± 1018	15 ± 1.5
0.2	16,062 ± 806	12 ± 1.2
0.5	7253 ± 318	03 ± 0.2
1.0	6739 ± 285	01 ± 0.1
2.0	5865 ± 235	≤0.1
4.0	659 ± 32	<0.1
6.0	431 ± 18	<0.1
8.0	317 ± 12	<0.1
10	106 ± 8	<0.1

'±' Standard deviation, $n = 3$.

concentration of HNO_3 whereas Ba^{2+} ions were not retained by the AMP-Al_2O_3 matrix beyond 2 M HNO_3. This indicated that Ba^{2+} ions could be eluted out using nitric acid of concentration >2 M while Cs^+ ions stays on the AMP-Al_2O_3 matrix.

However, at nitric acid concentration >2 M, the reaction conditions are highly corrosive and therefore the radioactive solution needs to be handled very carefully. It is desirable to have milder conditions for repeated operations in field conditions. Hence a combination of NH_4NO_3 and HNO_3 was used to determine the distribution of Cs^+ and Ba^{2+}, on similar lines. Table 4 depicts the distribution ratio values (K_d) of ^{137}Cs and ^{133}Ba using a combination of NH_4NO_3 and HNO_3.

It was observed that the presence of 0.1 M NH_4NO_3 enabled very good separation of Ba from the Cs, irrespective of the HNO_3 concentrations. However, further experiments were carried out using

Table 4
Distribution ratios (K_d) of Cs^+ and Ba^{2+} ions on AMP-Al_2O_3 in NH_4NO_3 + HNO_3 medium.

Adsorptive medium	Distribution ratio (K_d)	
	Cs^+	Ba^{2+}
0.1 M NH_4NO_3 + 0.1 M HNO_3	5879 ± 218	<0.1
0.1 M NH_4NO_3 + 0.2 M HNO_3	5621 ± 178	<0.1
0.1 M NH_4NO_3 + 0.3 M HNO_3	5590 ± 181	<0.1
0.1 M NH_4NO_3 + 0.4 M HNO_3	5371 ± 196	<0.1
0.1 M NH_4NO_3 + 0.5 M HNO_3	5296 ± 109	<0.1

'±' Standard deviation, $n = 3$.
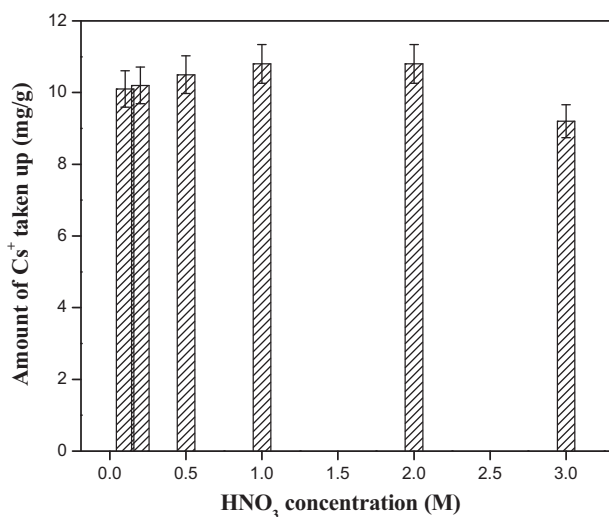
Fig. 3. Effect of HNO$_3$ concentration on Cs$^+$ uptake by AMP-Al$_2$O$_3$.

Fig. 4. Breakthrough profile of Cs$^+$ on passing CsNO$_3$ solution (1 mg Cs/mL) through a column containing 1 g AMP-Al$_2$O$_3$ at a flow rate of 0.25 mL min^{-1}.

0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ since the flow characteristic of eluent was best at this composition.

3.4. Determination of sorption capacity of AMP-Al$_2$O$_3$

3.4.1. Static sorption capacity

The uptake of Cs$^+$ by AMP-Al$_2$O$_3$ was studied as a function HNO$_3$ concentration and the results are shown in Fig. 3. Highest sorption capacity of Cs$^+$ by AMP-Al$_2$O$_3$ was found at 1 M HNO$_3$ and the capacity remained nearly constant up to 2 M HNO$_3$. At 3 M HNO$_3$ there was marginal decrease in capacity. The discrepancy between the K_d values and observed capacity values might be due to peptization of the gel particles at lower acidity. At acidity lower than 1 M HNO$_3$, slight swelling of gel particles took place due to peptization. This probably resulted in a lowering of capacity.

The maximum equilibrium capacity of this exchanger for Cs$^+$ was only in the range 10–12 mg g^{-1} which was ~10% of that obtained for pure AMP. From the result of the capacity determination by batch equilibration method it could be concluded that out of 16% of AMP trapped by alumina microspheres, only 10% was utilized for ion-exchange purpose. The remaining 6% of the AMP was probably trapped inside the spheres and not available for ion exchange. Although the capacity for Cs was low with the AMP-Al$_2$O$_3$ microspheres, it was adequate for generator application.

3.4.2. Breakthrough pattern and dynamic sorption capacity

The breakthrough curve developed in 2 M HNO$_3$ medium is depicted in Fig. 4. The curve had an S-shaped profile. From the curve, breakthrough capacity of AMP-Al$_2$O$_3$ for Cs$^+$ was found to be 4 mg g^{-1}. The feed solution containing cesium nitrate solution had a concentration 1.0 mg Cs mL^{-1} or 1.46 mg CsNO$_3$ mL^{-1} and the amount of sorbent packed in the column was 1 g. It was observed that up to 4 mL of the solution there was no breakthrough of ^{134}Cs, which corresponded to 4 mg of Cs. Therefore, ~4 mg of Cs per gram of the exchanger equivalent to 3.7 GBq (100 mCi) of ^{137}Cs could be loaded per gram of the AMP-Al$_2$O$_3$ microsphere without any breakthrough being observed.

The breakthrough capacity observed with this sorbent under dynamic conditions exhibited marked departure from the static capacity as a result of the impact of mass transfer limitations such as incomplete external film diffusion and/or to intraparticle transfer. The determination of the nature of the mass transfer resistance would require further studies, which are beyond the scope of this investigation. In the present case, the dynamic capacity was seen as
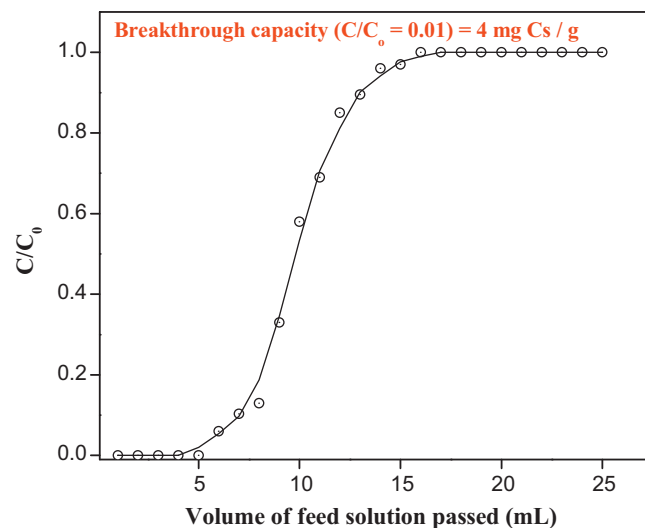
a criterion for retention capacity of the sorbent in the point-of-use system.

The flow rate of the feed solution through the chromatographic column should be optimized in order to ensure quantitative retention of ^{137}Cs. It was found that with the increase in flow rate from 0.1 to 0.5 mL min^{-1} cm^{-2} at a constant geometry of the column, the ^{137}Cs retention capacity practically remained same.

In order to optimize the volume of the feed needed for the loading of ^{137}Cs activity in the generator column, different volumes of sample solutions containing constant amount of Cs were passed through the column containing same amount of sorbent under identical geometry and operating conditions. The result obtained from such study is depicted in Table 5. The results of the ^{137}Cs sorption studies showed that the parent radionuclide could be efficiently retained (>95%) when sample volumes were less than 20 mL. In subsequent experiments, a sample volume of 10 mL was used for loading the ^{137}Cs activity in the column.

3.5. Elution of ^{137m}Ba from the AMP column

The elution profile of ^{137m}Ba using 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ solution is illustrated in Fig. 5. It was seen from the figure that the peak elution volume appeared at second fraction and most of the ^{137m}Ba could be eluted in 3 mL of the eluent. The generated ^{137m}Ba in the column is not significantly sorbed on AMP-Al$_2$O$_3$ microspheres and could be continuously eluted out.

Table 5
Effect of volume of the influent on ^{137}Cs loading.

Sample solution volume (mL)	Percentage of ^{137}Cs retention
5	98.6 ± 0.8
10	97.5 ± 1.5
15	96.8 ± 1.3
20	96.2 ± 1.5
25	94.7 ± 1.5
30	94.1 ± 1.6
35	93.7 ± 1.5
40	93.2 ± 1.5
45	93.2 ± 1.5

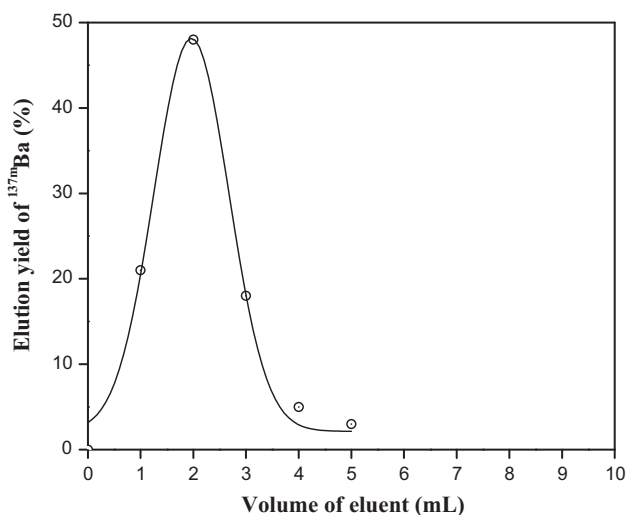'±' Standard deviation, n = 3.

Fig. 5. Elution profile of ^{137m}Ba from the AMP-Al$_2$O$_3$ column.

3.6. Process demonstration run

About 740 MBq (20 mCi) of ^{137}Cs activity in 2 M HNO$_3$, was quantitatively retained in the column. On washing with 100 mL of 2 M HNO$_3$ solution, only <0.5% of ^{137}Cs came out. This indicates that ^{137}Cs was strongly retained on the column. ^{137m}Ba was eluted from the column at different time intervals and elution yield is depicted in Fig. 6. The generator gave a consistent ^{137m}Ba elution yield between 80% and 85% (corrected for decay) over a period of 6 months. The elution efficiency of the generator was reasonably high and it did not deteriorate on repeated elutions over a prolonged period of time.

3.7. Quality control of ^{137m}Ba eluate

3.7.1. Radionuclidic purity

Both γ-spectrometry and half-life determination were used to determine the purity of the separated ^{137m}Ba. From the study of the decay profile of ^{137m}Ba, its half-life was determined to be ~2.5 min which is quite close to the theoretical value. The determination of contamination by the parent ^{137}Cs was made by counting the eluate after allowing the ^{137m}Ba to decay completely and by comparing this radioactivity with the original radioactivity at the time of elution. The amount of ^{137}Cs contamination present in the separated
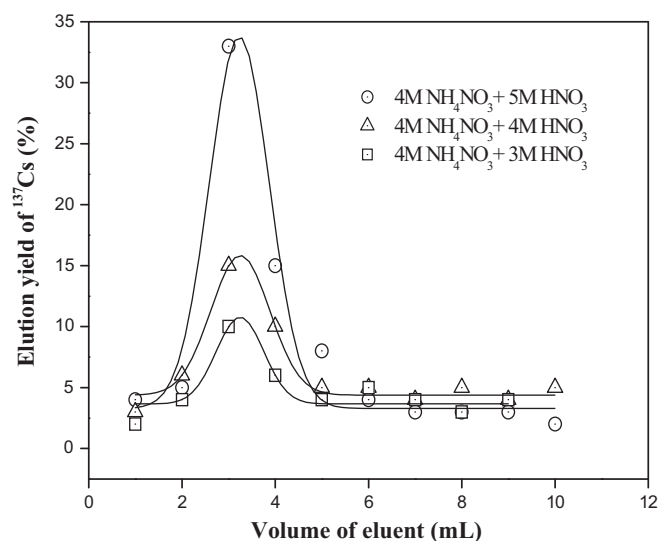

Fig. 6. Elution performance of the ^{137}Cs/^{137m}Ba generator. (a) Elution yield of ^{137m}Ba and (b) amount of ^{137}Cs in ^{137m}Ba.

Fig. 7. Elution profile of ^{137}Cs.

^{137m}Ba was estimated and depicted in Fig. 6. It was seen from the result that the ^{137}Cs contamination was between 0.005% and 0.01% of the original radioactivity. More than two hundred elutions or the passage of 1 L of eluent over a prolonged period of 6 months neither altered the product yield nor the purity.

3.7.2. Chemical purity

The chemical purity of the ^{137m}Ba eluate is important in many applications; therefore, the decayed eluates were analyzed for metallic impurities. Metal ion concentrations in 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ eluate were determined by ICP-AES technique. Al and Mo ions found in the ^{137m}Ba eluate were <10 ppm. These analyses showed that the eluate of the generator would not contaminate the process stream after radiotracer investigations.

The efficiency of elution was also unaffected by the frequency change in the elution. It is worthwhile to note that during the process demonstration run for a period of 6 months, no operational problems such as reduction of flow rate, head loss, packed bed compression and channeling of packed column were observed. Very long-term storage effects have not yet been investigated, but it seems that the system could be used over a long period of time because of the stability of this new sorbent and its exceptional selectivity for ^{137}Cs.

3.8. Recovery of ^{137}Cs from the spent generator

Cesium-137 retained by the exhausted column was recovered using a mixture of different concentration of NH$_4$NO$_3$ and HNO$_3$. The elution behavior of ^{137}Cs from the column is shown in Fig. 7. It is seen from the figure that the recovery of ^{137}Cs with 4 M NH$_4$NO$_3$ + 5 M HNO$_3$ was quite fast and nearly all the ^{137}Cs could be eluted out in 10–15 mL of the eluent.

Thus the granulated composite of AMP-Al$_2$O$_3$ proved to be effective for the preparation of ^{137}Cs/^{137m}Ba radioisotope generators. This process is extremely simple, rapid and provides a high recovery of ^{137m}Ba.

4. Discussion

Recently there has been a resurgence of interest in the use of ^{137m}Ba for industrial radiotracer technique. The major advantage of ^{137m}Ba lies in its accessibility from a ^{137}Cs/^{137m}Ba generator, which provides a non-reactor based and cost-effective source of

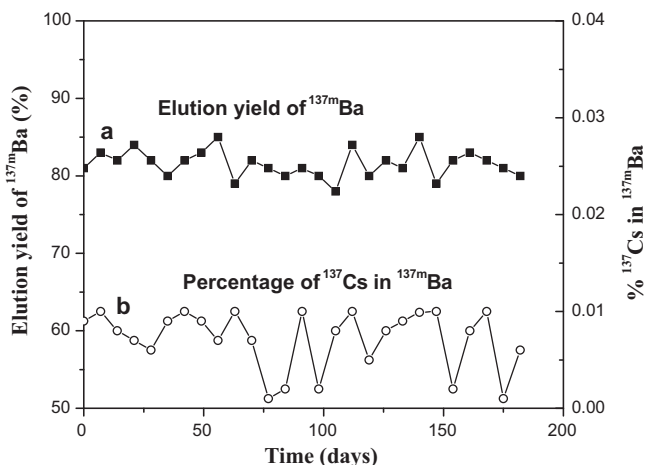short-lived radiotracer. The generator required for industrial application should offer radiochemically and radionuclidically pure ^{137m}Ba with high elution yield. The sorbent used should have chemical and radiation stability and provide ideal flow dynamics. The generator should be amenable for repeated elution over a prolonged period of time.

The commercially available ^{137}Cs/^{137m}Ba generators are of very low activity (typically 370 kBq), intended for the demonstration purposes in academic institutions and are exempted from specific State and Federal licensing for their use. Established radioactive source manufacturers including M/s Pasco, Roseville, CA 95747, USA, M/s Spectrum Techniques USA, Oak Ridge, TN 37830, USA, M/s Tel-atomic Inc., Jackson, MI 49204-0924, USA, etc. are supplying this generator worldwide in the form of kit. No technical information is available in the literature or internet about the details of the sorbent used by them, because of attached commercial interests. The need for a ^{137}Cs/^{137m}Ba generator amenable for industrial radiotracer investigation encouraged us to examine and re-evaluate the reported methodologies [5–15] explored by scientists throughout the world. The details of the generators studied during the last few decades with their limitations are provided in Table 6. A careful scrutiny of these reported works indicated that they have certain inherent limitations which restrict their applicability for making industrial ^{137}Cs/^{137m}Ba generators. Several issues related to the stability of the matrix in the presence of intense radiation environment, yield of ^{137m}Ba and its purity, amenability for repeated elution on long-term use and recovery of ^{137}Cs from spent generator are yet to be addressed. Concerted efforts are warranted to develop viable ^{137}Cs/^{137m}Ba generators using new class of sorbents to mitigate the limitation of reported techniques and to realize scope of utilizing the benefits of ^{137m}Ba for industrial radiotracer investigations. In the quest for an effective sorbent, we have focused our interest towards AMP-Al$_2$O$_3$, an engineered form of AMP, as it offers the selectivity towards ^{137}Cs while maintaining good flow characteristics for propitious outcome. In the reported method, we have used internal gelation procedure to avail AMP-Al$_2$O$_3$ microspheres of good granulometric properties amenable for column operations.

The phosphomolybdate complex ion (PMo$_{12}$O$_{40}$)$^{3-}$ is reported to consist of a hollow sphere formed by the 12 MoO$_6$ octahedra with the PO$_4$ group in the center of the crystal structure of the ammonium salt of this ion [18]. It has a structure riddled with pores and tunnels [23] in which the ammonium ions with associated water molecules are fitted in between the spheres of negative ions. The uptake of Cs$^+$ ions in AMP takes place due to isomorphous exchange of Cs$^+$ ions for NH$_4^+$ ions in the crystal lattice [40]. The exchange of Cs$^+$ ions is preferred due to the small size of the "hydration sphere" of Cs$^+$ ions. The ions with the smaller radii can easily enter the pores of the exchanger [18]. The "hydrated" Ba^{2+} ion is quite large compared to the less hydrated Cs$^+$ ion, and cannot get bound to the deep seated negative charges in the AMP matrix. The ^{137m}Ba^{2+} species formed upon decay of the ^{137}Cs gets eluted as the open porous structure of AMP favors facile release of this ion by diffusion.

Our initial aim was to load nearly quantitative amount of ^{137}Cs activity in the column with minimum release of activity into the effluent while maintaining a reasonable flow rate. During the process of ^{137}Cs loading, the acidity of the feed solution was kept at 2 M HNO$_3$, a need arising on account of the tendency of the sorbent to peptize at low acidity and to obtain satisfactory flow rate during activity loading. The high distribution ratios (K_d) value for Cs$^+$ and negligible distribution ratios (K_d) value for Ba^{2+} at 2 M HNO$_3$ allowed realistic loading of ^{137}Cs activity in the column. Though the results of distribution ratios (K_d) values permit satisfactory elution of ^{137m}Ba in 2 M HNO$_3$, the use of this solvent restricts the utility of the generator for industrial applications. The reaction conditions

at 2 M HNO$_3$ are corrosive and often undesirable in field conditions from environmental or safety perspectives. It was envisaged that judicious selection of a milder eluting reagent would mitigate the consequence of using 2 M HNO$_3$ and render the process amenable for field conditions. Instead of 2 M HNO$_3$, a mixture of the NH$_4$NO$_3$ and HNO$_3$ was hence considered worthwhile investigating to arrive at the optimum condition for eluting ^{137m}Ba of desirable quality with appreciable yield.

It has been reported [19] that Ba^{2+} ion can get exchanged with the NH$_4^+$ ions of AMP provided it exists as Ba(OH)$^+$, according to the mechanism

$$Ba^{2+} + H_2O \rightleftharpoons Ba(OH)^+ + H^+$$
$$RNH_4 + Ba(OH)^+ \rightleftharpoons RBa(OH) + NH_4^+$$
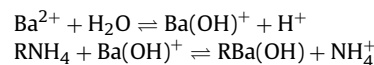
where R is a molybdophosphate anion. This reaction scheme explains the dependence of the sorption of Ba^{2+} on the concentration of NH$_4^+$ ions as well as on the acidity of the medium. The rationale of using the composition 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ is that NH$_4^+$ content in this combination is just adequate to elute only ^{137m}Ba be present in the column, but not ^{137}Cs. During the elution with 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$, a species such as Ba(OH)$^+$ is very unlikely to exist [41] and ^{137m}Ba gets eluted out easily with high yield. On the other hand, insignificant co-elution of ^{137}Cs could be attributed to a probable stable chemical link of the ^{137}Cs species with the AMP. Working with 0.1 M NH$_4$NO$_3$ + 0.5 M HNO$_3$ also has the advantage of maintaining high flow rates.

A lead shielding assembly has been used to house the generator assembly column to minimize radiation exposure. The lead shielding assembly has been designed in such a manner that minimal handling is required for eluting ^{137m}Ba out of the generator column. The design also provides a means of safe, effective, and reliable transfer of ^{137m}Ba under closed conditions.

In order to use ^{137m}Ba for radiotracer application, impurities of ^{137}Cs have to be limited as that may lead to abnormal result caused by the continuing production of ^{137m}Ba due to the decay of ^{137}Cs with its relatively long half-life. Therefore, it is essential to check the level of ^{137}Cs impurities in the separated product. Process demonstration run was carried out using 0.74 GBq (20 mCi) of ^{137}Cs with the goal of assessing the efficacy of the generator in the presence of intense radiation environment with the radiolytic products generated as a result of radioactive ^{137}Cs, to deliver ^{137m}Ba of acceptable purity on repeated use for long-term operation. The generator gives consistent elution yield of ^{137m}Ba without sacrificing the purity.

The ^{137}Cs parent radionuclide is very long lived ($T_{1/2}$ = 30 years); hence the generators theoretically have a very long life-time. However, leaving ^{137}Cs in a column matrix any longer than necessary can lead to substantial radiation degradation of the column matrix and hydrodynamic problem, which often results in breakthrough of ^{137}Cs in the ^{137m}Ba eluate. Thus the generator developed should allow elution of the ^{137}Cs parent after every year of operation. Hence, procedure for removing ^{137}Cs from the generator column was pursed. Moreover the spent generator columns cannot be discarded without removing the radioactive ^{137}Cs from the generator column and therefore removal of ^{137}Cs from the column prior to disposal was also important from the waste-management point of view. Additionally, it is economical to salvage ^{137}Cs from the spent generator prior to disposal as the radioactivity can be reused for the preparation of a new generator.

Although the capacity of AMP-Al$_2$O$_3$ for Cs$^+$ was low compared to other engineered forms of AMP, it was adequate for generator applications. The major benefits of AMP-Al$_2$O$_3$ are (i) rapid packing due to the high density of the sorbent which settles in a few minutes, (ii) rigidity which allows the use of high flow rates and (iii)

Table 6
The reported methods for the preparation of $^{137}Cs/^{137m}Ba$ generator.

Ref. No	Researcher(s)	Column material	Eluent	Elution yield (%)	Remarks
5	Pinajian	Zirconium phosphate	1 M HCl	20	Low elution yield
6	Blau	AMP + asbestos (1:1)	0.1 M HCl	50	Low elution yield
7	Nagal and Watari	Metal ferrocyanide loaded resin	0.9% NaCl	60	Low elution yield
8	Bonnin et al.	Cupric ferrocyanide	$Ba(NO_3)_2$ Solution	20	Low elution yield
9	Kawashima	Cupric ferrocyanide	Water	40–60	Low elution yield
10	Prout	Potassium hexacyano cobalt (II) ferrate (II)	–	–	Instability of the sorbent in aqueous solution restricts its utility.
11	Dhara et al.	$Na_2(H_2O)_4(H_3O)[Al(OH)_6Mo_6O_{18}]$	–	Not reported	Neither provide any information about the elution yield of ^{137m}Ba nor the long term use of the generator.
12	Maji and Basu	Chelating resin	–		
13	Wang et al.	Cupric cobaltic ferrocyanide	0.1 N HCl + 0.9% NaCl	93–42	Although the elution yield of ^{137m}Ba was reported to be ~90% at the beginning, it decreases appreciably in subsequent elution and reaches up to 42% after 15 elutions.
14	El-Absy et al.	Tungstocerate	0.1 N HCl + 0.9% NaCl	68	Although effective, the utility of this generator is yet to be tested at higher activity level typically used in an industrial generator.
15	Koprda and Scasnar	Beads loaded with dicarbolide-H$^+$	$NaCl–HNO_3$ solution of pH 4	65–70	Long-term stability of the extraction-chromatographic system under repeated elution is debatable.

^{137}Cs bleeding was negligible due to the stable chemical link of the ^{137}Cs species with the AMP.

The objective of developing industrial scale $^{137}Cs/^{137m}Ba$ generator with simplified procedure to elute ^{137m}Ba in high yields, commensurate with industrial tracer investigations, has been achieved. Consistently high elution yields of ^{137m}Ba ($\geq$80%) with acceptable purity were obtained over a prolonged period. It is important to note that, during the process demonstration run, the flow performance was excellent, no noticeable fines were observed in the product, and no column operational problems were encountered. Availability of generator in a shielded enclosure facilitates its transport to the radiotracer investigation site. The process of making the generator is simple and cost involved is modest. The successful development of industrial scale $^{137}Cs/^{137m}Ba$ generator, which met industry specifications, is a significant step towards the availability of ^{137m}Ba for radiotracer investigation. It is envisaged that the reported method would serve in good stead for ensuring the easy availability of ^{137m}Ba for industrial radiotracer investigations. The prospect of using this $^{137}Cs/^{137m}Ba$ generator to obtain ^{137m}Ba appears promising in countries having active industrial radiotracer program and not having access to operational research reactors for radioisotope production.

5. Conclusion

This study demonstrates the usefulness of AMP-Al_2O_3 for the development of $^{137}Cs/^{137m}Ba$ chromatographic column generator for industrial radiotracer investigations. The optimum condition for sorption of ^{137}Cs in the column was found in 2 M HNO_3. Barium-137m could be eluted from the generator in 0.1 M NH_4NO_3 + 0.5 M HNO_3 with >80% yields and with high radionuclidic and chemical purity. The sorbent has been successfully utilized in the preparation of a 0.74 GBq (20 mCi) $^{137}Cs/^{137m}Ba$ generator and its performance was evaluated for 6 months in which ^{137m}Ba of requisite purity could be consistently availed with >80% yield. Availability of $^{137}Cs/^{137m}Ba$ radionuclide generators will help the radiotracer community to harvest the beneficial use of ^{137m}Ba radiotracer for routine services to industry and environment. It is anticipated that the production cost of an industrial $^{137}Cs/^{137m}Ba$ generators will be significantly lower than the medical ones, as stringent pharmaceutical regulatory requirements are not needed for industrial applications.

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